

Combustion Research Facility NEWS



Hydrogen-Enriched Lean Premixed Combustion Makes Ultra-Low Emission Gas Turbine Combustors Possible

Prompted by the need for cleaner burning fuels, Sandians are exploring advanced combustion capabilities for hydrogen and hydrogen-blended hydrocarbon fuels in gas turbine engines. Bob Schefer and Joe Oefelein are investigating these capabilities with a newly designed and assembled swirling-flow dump combustor (see Figure 1). They are using the combustor to examine changes in fuel composition, particularly with the addition of hydrogen to hydrocarbon fuels, which affect both the chemical and physical processes occurring in flames. These changes in turn affect flame stability, pollutant emissions, combustor efficiency and other important quantities. Few of these issues are clearly understood.

Swirling-Flow Dump Combustor

The swirling-flow dump combustor was designed for modeling and model validation using the large eddy simulation (LES) technique. The design has been optimized to provide unambiguous boundary conditions required for the validation of high-fidelity LES simulations, while making optimal use of the advanced diagnostic capabilities developed at the CRF.

The baseline configuration of the combustor generically emulates the fluid dynamic, thermodynamic, thermochemical and transport processes that occur in typical industrial gas turbine combustors. An annular premixed fuel-air jet is injected through a set of swirl vanes into an expansion chamber. The gas mixture (methane enriched with hydrogen) inside the injector is acoustically insulated and conditioned in a manner that provides a fully developed, swirling turbulent velocity profile at the injector exit. The swirler produces this profile with a uniform equivalence ratio, a uniform mass flow rate

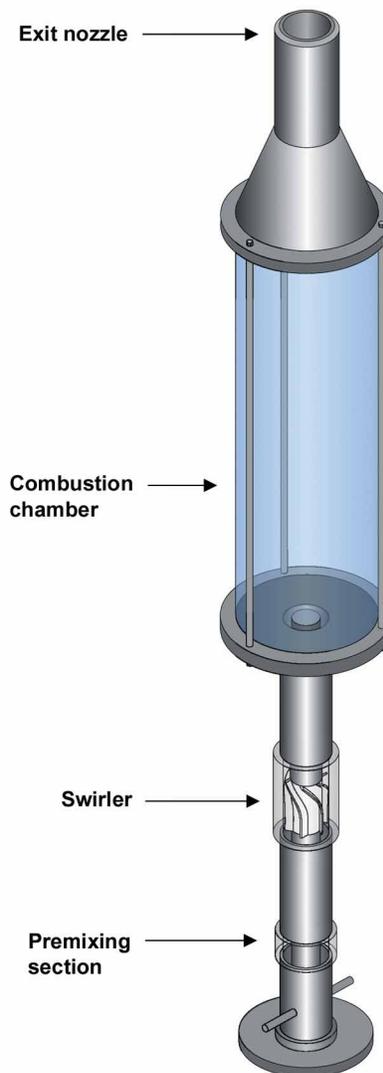


Figure 1. Schematic of the CRF swirling-flow dump combustor designed to study combustion of hydrogen and hydrogen-blended hydrocarbon fuels.

and diminished wake effects. The quartz cylindrical chamber is designed to provide clean, diagnostically accessible swirling flames without complicating factors such as wall impingement effects. The nozzle provides a constant-pressure exit boundary condition, with zero axial gradients.

The premise for this work is that ultra-lean premixed combustion effectively reduces NO_x emissions from gas turbine engines, but has difficulty maintaining flame stability because of the low flame temperatures required to reduce NO_x . Blending hydrogen with traditional hydrocarbon fuels used during ultra-lean combustion significantly improves flame stability, while still allowing the low temperatures needed to minimize NO_x . Success in this work will bring researchers one step closer to the ultimate goal of a carbon-free energy system.

Testing and Verification

To determine the effects of hydrogen addition on flame stability, burner stability characteristics were also studied. Figure 2 shows details of flame blowout characteristics under fuel-lean conditions. Generally, the flame blowout velocity decreased as the fuel/air ratio became leaner. In this study, various amounts of hydrogen were added to the methane/air mixture, and the flame stability measurements were repeated. The results showed that hydrogen significantly increased flame stability.

Verification of the experimental configuration is ongoing and focuses directly on issues related to the validation of LES subgrid-scale models. A series of LES calculations were performed to corroborate the existence of well-posed boundary conditions and relevant flow characteristics.

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Novel Master Equation Analysis Validates Key Role of C_3H_3 Recombination Reaction in Soot Formation Process

The cyclization of linear hydrocarbons, to form an aromatic ring compound such as benzene, is the rate-limiting step of soot formation in flames of aliphatic fuels. The recombination of propargyl radicals is widely believed to provide the dominant cyclization pathway. However, little is known about the kinetics of this process, particularly at combustion temperatures.

In a recent detailed theoretical analysis of this reaction, Sandians Jim Miller and Stephen Klippenstein validated prior empirical models such as that of Miller and C.J. Pope. They also reaffirmed the importance of the propargyl recombination reaction in soot formation.

Previous experimental studies have generally probed only rate and product distributions of the reaction from room temperature to 675 K. In pioneering theoretical work at the CRF, Miller and Carl Melius examined the potential-energy surface for this reaction with bond-additivity corrected perturbation theory. While this approach does not provide quantitative kinetic predictions, their work yielded substantial insight into the reaction, most notably demonstrating the presence of a pathway to benzene that has no barriers above that of the entrance channel.

Calculating Rate Coefficients

Theoretically predicting the rate coefficient and product distribution for the $C_3H_3 + C_3H_3$ reaction is a daunting task because of the multiple, interconnected wells on its potential energy surface. However, Miller and Klippenstein have recently derived an approach for extracting phenomenological rate coefficients for such complex reactions by using solutions of the master equation. They have now applied this approach to the analysis of the C_3H_3 recombination reaction,

employing RRKM evaluations of the microcanonical rate coefficients. In the course of this work, these researchers also reexamined the stationary points on the potential-energy surface with high-level quantum chemical simulations and discovered an additional cyclization pathway.

Sandians Jim Miller and Stephen Klippenstein have reaffirmed the importance of the propargyl recombination reaction in soot formation.

Key Test

An experimental study of the product distribution for the pyrolysis of 1,5 hexadiyne, done at the National Institute of Standards and Technology by S.E. Stein and coworkers, provides a key test for Miller and Klippenstein's theoretical model. The

successful reproduction of experimental data (see Figure 1) relies on the improved quantum chemical estimates and, even more significantly, on the new cyclization pathway, which ultimately proved to be the dominant reactive pathway under combustion conditions. Miller and Klippenstein also validated Pope and Miller's kinetic modeling study of benzene formation in the flames of aliphatic fuels by producing a remarkably similar rate coefficient for the C_3H_3 reaction (see Figure 2). At 1500 K and 1atm, the rate coefficient was predicted to be $1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, while the empirical value employed by Pope and Miller was $1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The similarity of the rate coefficients confirms Pope and Miller's kinetic modeling study. Pope and Miller employed a rough estimate for the C_3H_3 recombination rate coefficient in their kinetic modeling of the flames of aliphatic fuels. While this kinetic model yields good agreement with many aspects

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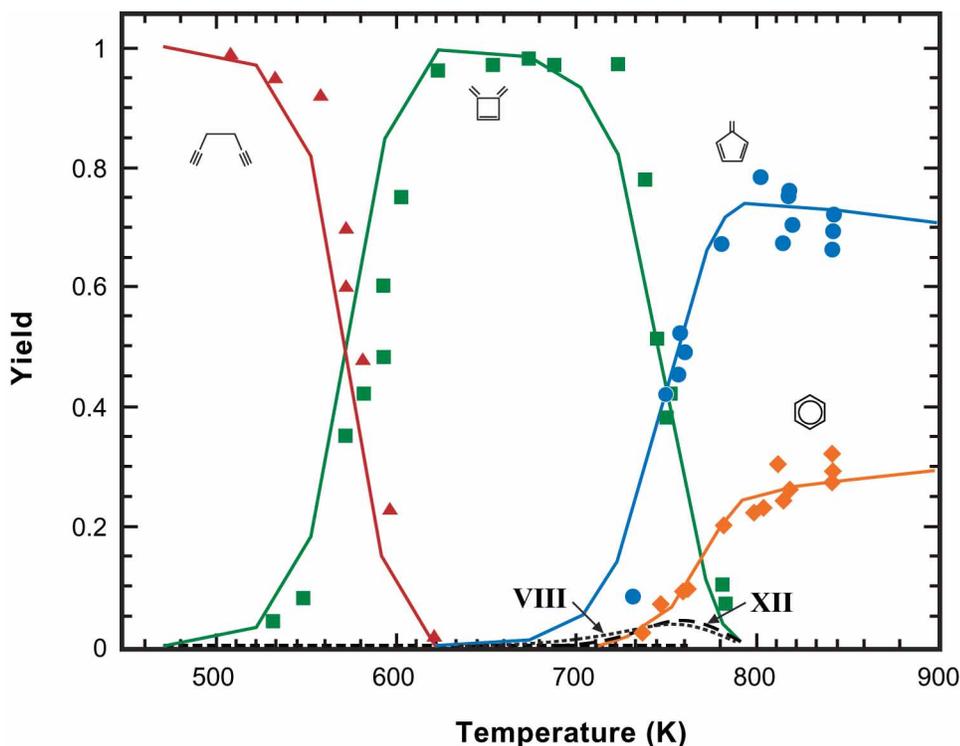


Figure 1. Product yields as a function of temperature in the pyrolysis of 1,5 hexadiyne. VIII and XII denote two rotamers of 1,3 hexadiene-5-yne. The symbols denote the experimental data of Stein and coworkers; the lines denote Miller and Klippenstein's theoretical predictions.

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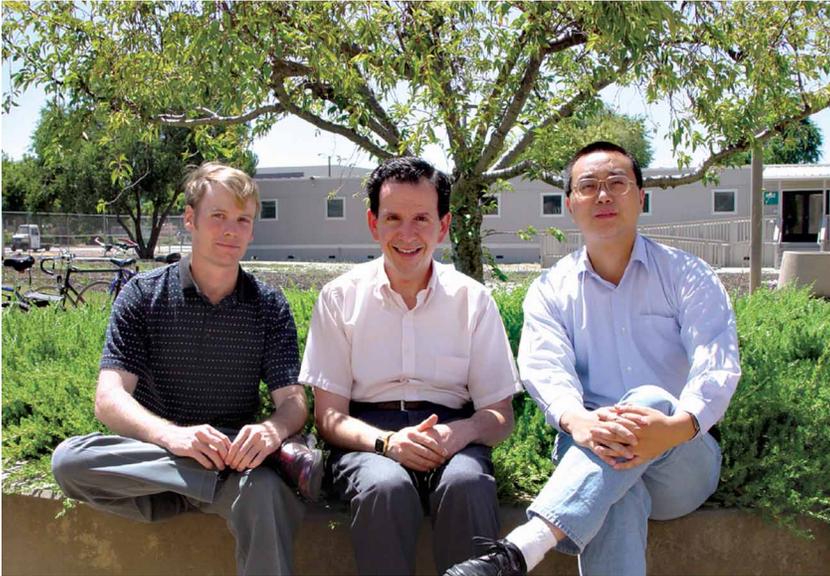
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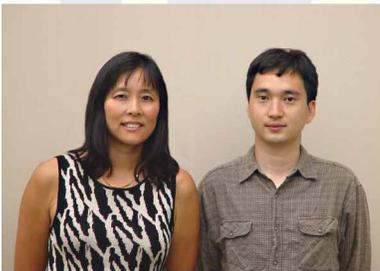


Mark Allendorf Elected Electrochemical Society Vice President

Mark Allendorf has been elected vice president of The Electrochemical Society (ECS), an 8,000-member international society devoted to solid-state and electrochemical science and technology. After serving in this position for three years, he will become president. Allendorf became an ECS Fellow last year and has been an ECS member for 17 years. His research focuses on industrial processes involving high-temperature chemistry at interfaces.

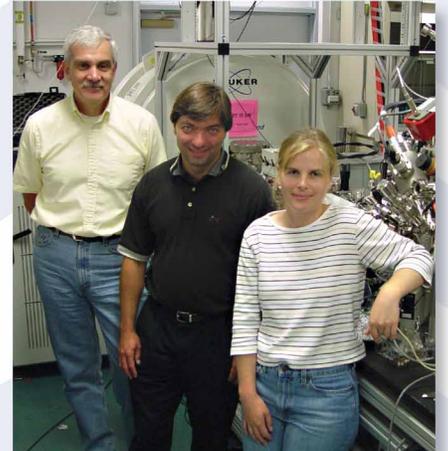


For the past two years, Yuan Zheng (right) and Allen Ricks (left) from Purdue University have been working with Alan Kerstein (middle), Scott Wunsch and Bill Ashurst on fire modeling. Zheng and Ricks are Ph.D. students in mechanical engineering, specializing in combustion. Also contributing to this ongoing modeling effort are Sheldon Tieszen and John Hewson from Sandia's Albuquerque, N.M., site.

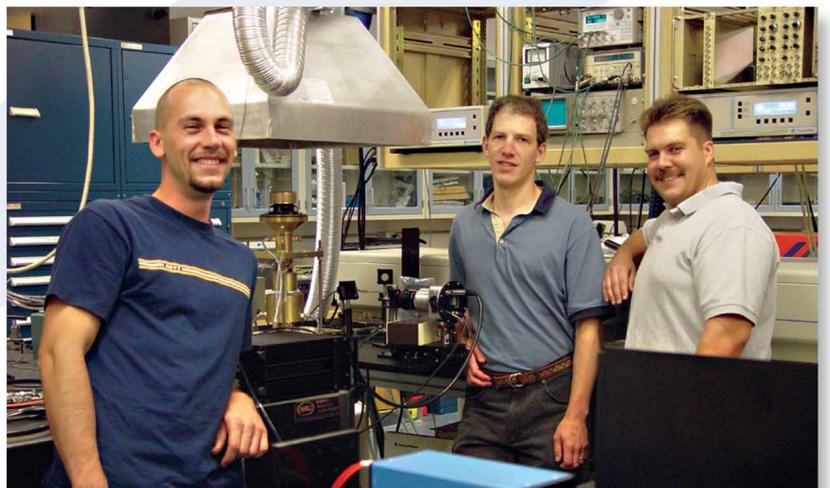


Lijun Song (right), a mechanical engineering graduate student at Purdue University, worked with Jackie Chen (left) for two months on direct numerical simulation (DNS) of opposing flames. Song, who is specializing in diesel engine combustion, has also been learning the DNS code.

People

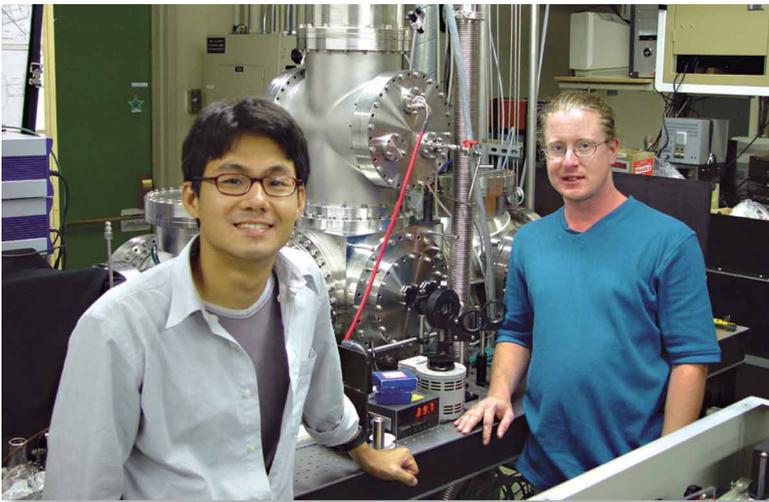


Postdoc Saskia Hoffer (right) has left the CRF to become a staff member in Sandia's neutron generator production facilities in Albuquerque, N.M. For the past year, she has worked with Gary Kruppa (middle) and Rich Behrens (left) studying energetic materials using mass spectrometry.



A Ph.D. student from Yale, Giuliano Amantini (left) worked at the CRF this summer investigating vortex flame interactions and counterflow diffusion flames. Amantini was hosted by Jonathan Frank (middle), and also worked with Ron Sigurdsson (right). Amantini's advisors on this project at Yale are professors Mitchell Smooke and Alessandro Gomez.

People People



Wei-Bin Lee (left) visited the CRF this summer to work with Bradley Parsons (right) and David Chandler on reactive scattering and photochemistry of bromine compounds. The focus of this project was to determine the relative reactivity of ground state or spin-orbit excited atomic chlorine with molecular hydrogen using cross-beam scattering with ion imaging. Lee is studying photochemistry of bromine-containing compounds at the Institute of Atomic and Molecular Sciences in Taiwan.



Stewart Cant (left), a long-time CRF collaborator, visited for a month this summer to study scalar transport in premixed turbulent hydrogen/air flames with Jackie Chen (right). Cant is a professor in the Department of Engineering at Cambridge University in England.



Fred Gouldin (middle right), of Cornell University and Chris Lawn (middle left), of the University of London completed six-month sabbaticals at the CRF in July. The professors worked with Sandians Bob Schefer (right) and Joe Oefelein (left) on turbulent reacting flow.

Jose Javier Lopez Sanchez (right) examined the effects of wall impingement on soot processes in diesel fuel jets this summer with his host, Lyle Pickett (left). Lopez Sanchez visited the CRF from the University of Valencia in Spain where he is an assistant professor in the Mechanical Engineering Department.



Hosted by Ray Bambha (left), Uwe Lehmann (right) visited from the University of Applied Sciences in Berlin, Germany. Together they worked on infrared light source development for a spectrometer that measures isotopes of greenhouse gases.



Patrick Flynn (right), retired vice president of research at Cummins, Inc., recently visited the CRF to work with Richard Steeper (left) and Andy Lutz (middle) in exploring the use of hydrogen fuels in internal combustion engines as part of the U.S. Department of Energy's FreedomCAR initiative. Flynn has a long history of interaction with the CRF, as a collaborator with the CRF's engine research group and as a member of the CRF Advisory Board.

Combustor

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Having established the appropriate boundary and operating conditions, attention is now focused on validation. As part of a new workshop series entitled International Workshop on Modeling and Validation of Combustion in Gas Turbines (CGT), researchers will

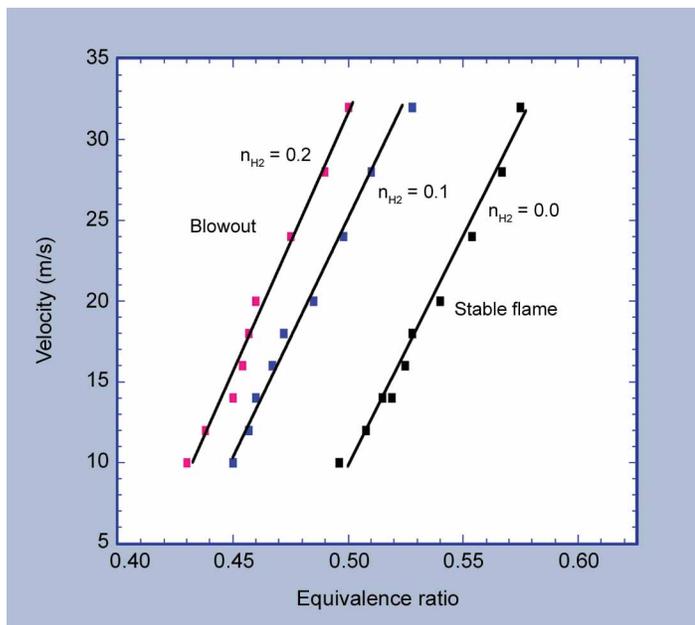


Figure 2. Effect of hydrogen addition on lean stability limits in premixed swirl-stabilized flame. The three curve fits through the data are for volumetric fractions of hydrogen in the fuel of 0 (pure methane), 0.1 (10% hydrogen) and 0.2 (20% hydrogen). A stable flame can be maintained to the right of each curve and flame extinction occurs to the left.

focus on developing a consolidated series of target cases relevant to gas turbine combustion (see www.ca.sandia.gov/CGT/). Using the International Workshop on Measurement and Computation for Turbulent Nonpremixed Flames (TNF) as a model (see www.ca.sandia.gov/TNF/abstract), collaborative comparisons of measured and modeled results will lead to a better understanding of the limitations of various modeling approaches for gas turbine combustion.

Representative results are shown in Figure 3. On the left is a planar laser-induced fluorescence image of the OH molecule (OH PLIF) that highlights the structure of a lean premixed flame in the swirl burner. On the right is the corresponding instantaneous velocity field obtained using LES. At the conditions shown, diverse local flame structures are observed throughout the combustor. The LES calculations performed to date have produced similar qualitative trends. Detailed quantitative validation will progress systematically in future studies.

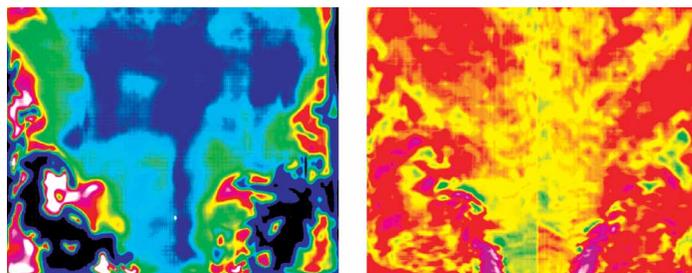


Figure 3. Experimentally measured OH PLIF image (left) and instantaneous velocity field (right) calculated using LES. The images reveal the complex flow and flame structure in a lean premixed swirl-stabilized burner.

Analysis

(Continued from page 2)

of the observed species concentration there was considerable uncertainty in the value employed for the C_3H_3 recombination rate coefficient. Miller and Klippenstein's current work provides an *a priori* fundamental theoretical prediction for this rate coefficient, which is in remarkable agreement with the empirical value previously employed by Pope and Miller. At 1500 K and 1 atm, the rate coefficient was predicted to be $1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, while the empirical value employed by Pope and Miller was $1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The similarity of these rate coefficients confirms this key aspect of Pope and Miller's kinetic modeling.

Overall, Miller and Klippenstein's theoretical study lends strong support to the importance of the $C_3H_3 + C_3H_3$ reaction as the first cyclization step along the pathway to soot formation under a wide range of conditions.

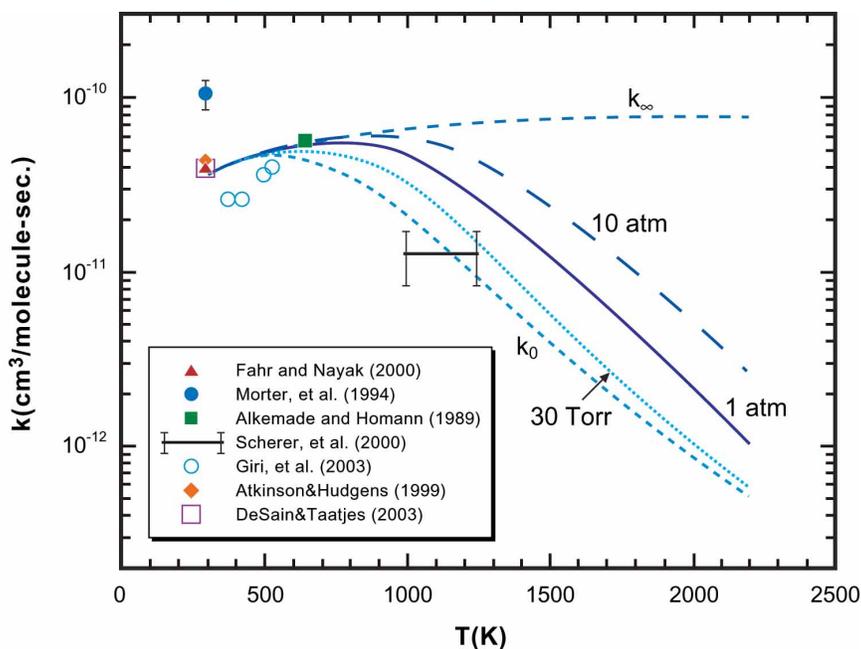
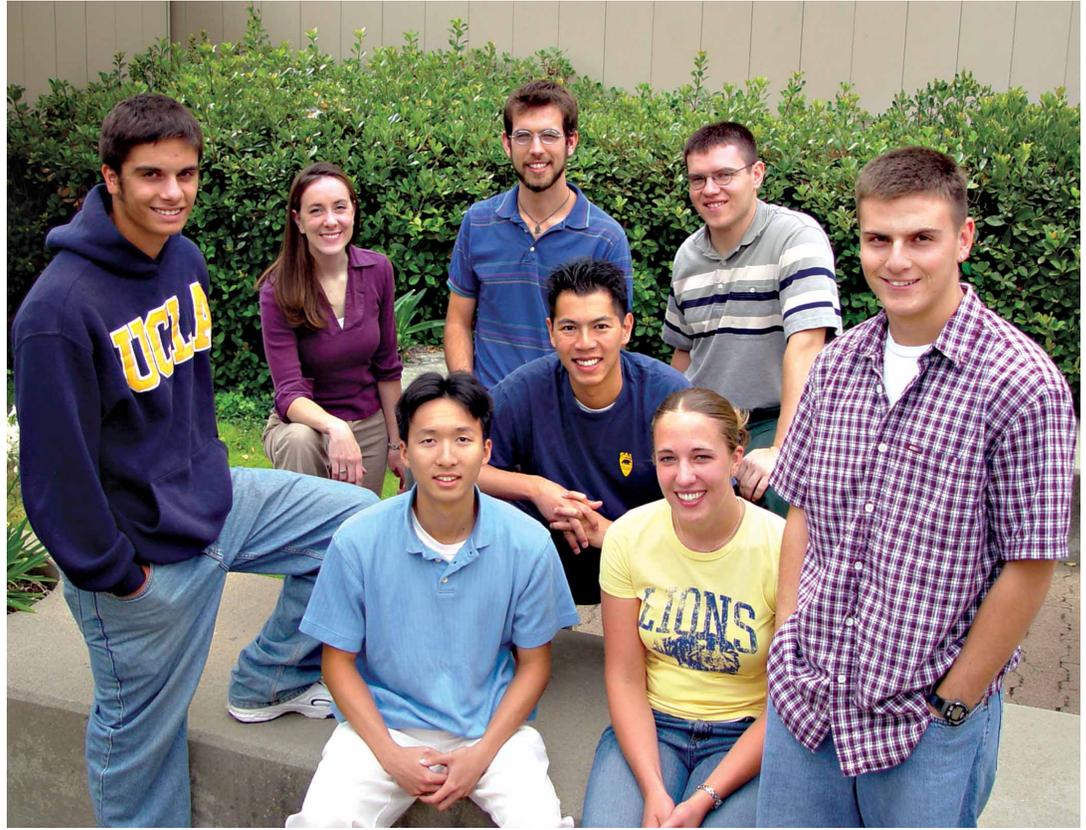


Figure 2. Total rate coefficient for the reaction $C_3H_3 + C_3H_3$ products as a function of temperature and pressure. All lines, except Scherer's, denote theoretical predictions of Miller and Klippenstein.

2003 Summer Student Interns Assist Mentors in Variety of Disciplines

Twelve interns held a variety of positions this summer at the CRF, participating in activities such as modeling hydrogen power parks, synthesizing protein crosslinkers, predicting reaction rates for many species using CHEMKIN and redesigning the CRF Web site. The interns represented a variety of schools and majors, including engineering, history, nursing and English.



Last Chance to Rate the CRF News

If you haven't yet submitted your CRF News reader survey, here's your chance. You can find the survey at www.ca.sandia.gov/CRF/03_news.html until Sept. 30. We would very much like to hear what you think!

From left to right: (top row) Chris Behrens of University of California at Los Angeles, Natalie Cherry of Brigham Young University (BYU), Carl Mas of University of California at Berkeley, Brent Pickett of BYU; (bottom row) Edward Jan of Cornell University, Andrew Ho of the University of California at San Diego School of Medicine, Kelsey Nyholm of BYU and Alec Barlow of California Polytechnic State University. Not pictured: Michael Thielvoldt of Stanford University, Erin Nyholm of Livermore High School, Andrew Madewell of the University of Arizona, Janine Scott of Las Positas Community College, and Alexander Murray of Granada High School.

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